AD-A052 955 CHICAGO UNIV ILL F/G 7/4
LASER SPECTROSCOPIC TECHNIQUE.(U)
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UNCLASSIFIED AFOSR-TR-78-0677 NL

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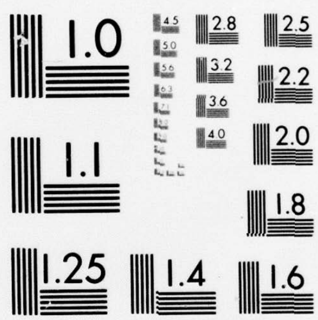

MICROCOPY RESOLUTION TEST CHART
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Final Report

Initial Date: June 1, 1975
Final Date: November 30, 1977

AFOSR 75-2853

See 1473

"Laser Spectroscopic Technique"

The major accomplishments achieved in the performance of this research effort are as follows:

(1) The design, development and exploitation of first and second generation apparatus for studying the spectroscopy of ultra cold molecules by laser induced fluorescence. This technique was the first joining of supersonic jets and laser optical spectroscopy for the simplification of complex optical spectra, for the observation of new van der Waals molecules, and for the observation of photo chemical processes

(2) The fluorescence excitation spectrum of NO_2 was measured in the region 5708–6708 Å using a tuneable dye laser as an excitation source. The NO_2 was cooled to a rotational temperature of ~ 3 K by expansion with argon as a carrier gas through a supersonic nozzle. This cooling drastically reduced the rotational structure and thereby permitted a clear separation and analysis of 140 vibronic bands found in this 1000 Å region of the spectrum. The results indicate that most of the fluorescence in this region is due to a $^2B_2$ electronic state, and that this state is so heavily perturbed by high levels of the ground electronic state that a substantial fraction of all ground state levels of appropriate vibronic symmetry in this region have appreciable fluorescence intensity.

(3) The HeI_2 van der Waals complex was prepared from a dilute mixture of iodine in helium at a pressure of 100 atm by supersonic expansion through a nozzle into a vacuum. Laser-induced fluorescence excitation spectra were recorded for the $\tilde{B} \leftarrow \tilde{X}$ transition of HeI_2 as well as corresponding spectra for the He_2I_2 and I_2 molecules in the expanding gas. I_2 was found to be cooled by the expansion to a rotational temperature of 0.4 K, and a vibrational temperature of 50 K. Similarly cold internal temperatures were attained by the van der Waals complexes. Evidence was found for vibrational predissociation of the HeI_2 complex in both the $\tilde{X}$ and $\tilde{B}$ electronic states. The vibrational predissociation rate was found to depend weakly upon the degree of excitation of the I-I stretching mode, ν_1. For $\nu_1 = 1$ in the $\tilde{X}$ state the predissociation rate was found to be greater than $5 \times 10^{6}\ s^{-1}$. In the $\tilde{B}$ state the vibrational predissociation rate is $\sim 5 \times 10^{10}\ s^{-1}$ for $\nu_1 = 27$, decreasing to $< r \times 10^{9}\ s^{-1}$ for $\nu_1 \leq 7$. The small (3.4–4.0 cm^{-1}) blue shifts of the vibronic bands of the HeI_2 spectrum relative to corresponding bands of I_2 indicate (1) the van der

Waals complex is slightly more strongly bound in the $\tilde{X}$ state than it is in the $\tilde{B}$ state, and (2) the I-I bonding in both the $\tilde{X}$ and $\tilde{B}$ states of iodine is largely unaffected by the formation of the van der Waals bond with helium.

(4) The spectrum of the $HeNo_2$ molecule was identified as a weak broad feature $\sim 1.5\ cm^{-1}$ to the high frequency side of the R (0) line of the NO_2 vibronic origin. The $\sim 0.8\ cm^{-1}$ width is due to lifetime broadening, $\sim 10^{-11}$ seconds, and must be due to the dissociation of the complex.

(5) The vibrational energy distribution in the photodissociation products of HeI_2 has been shown to obey the propensity rule $\Delta\nu = -1$ by observation of fluorescence of the daughter I_2.

(6) The van der Waals molecule NaAr has been prepared in a supersonic expansion of sodium vapor plus a few percent argon in a helium carrier gas. The fluorescence excitation spectrum of the $X^2\Sigma^+ \rightarrow A^2\Pi$ optical transition has been analyzed and the vibrational and rotational spectroscopic constants have been derived from this analysis. The ground state interatomic potential implied by these parameters is consistent with that measured or calculated by other workers. The observed Λ-doubling of the $A^2\Pi$ state suggests that the coupling between the $A^2\Pi$ and $B^2\Sigma$ states may be stronger than would be expected from previous calculations. The magnitude and sign of the dependence of the fine-structure splitting of the $A^2\Pi$ state on vibrational quantum number suggests that the van der Waals bond produces an observable perturbation of the core electrons of the sodium atom.

(7) The fluorescence excitation spectrum of the $^1B_{3u}\ (\nu' = 0) \leftarrow {}^1A_g\ (\nu'' = 0)$ transition in s-tetrazine has been observed and measured. The sample was cooled to a rotational temperature of <1K by expansion in a supersonic free jet. In this way the rotational structure arising from asymmetry split low J lines could be observed. The rotational A and B axes of the $^2H_1\,{}^{12}C_2\,{}^{14}N_4$ isotope were observed to interchange upon electronic excitation and a theory describing the effect of this interchange upon the optical selection rules has been developed. Analysis of the resolved rotational structure suggests that the geometry change upon electronic excitation is smaller than that deduced from previous analysis of the room temperature optical spectrum.

(8) The vibrational relaxation of I_2 by H_2 has been studied in a supersonic free jet. It was observed that the addition of 5% H_2 to the helium carrier gas greatly reduces the concentration of $X^1\Sigma_g^+\ (\nu'' = 1)\, I_2$ in the jet as compared to the concentration in a pure helium carrier. From this observation we have determined that the average vibrational relaxation cross sections of H_2 is 7.1 times as large as that of helium. Since the average vibrational relaxation cross section of H_2 is 7.1 times as large as that of helium. Since the average vibrational relaxation cross section of deuterium is at least as large as that of hydrogen, the mechanism responsible for this phenomenon appears not to be dominated by mass effects.

(9) The 0-0 band of the $B \leftarrow X$ visible spectrum of iodine has been observed in spite of its very small Franck-Condon factor. The expected satelite band of the van der Waals molecule HeI_2 was not observed, and a mechanism is suggested to account for the absence of the van der Waals spectrum.

(10) The rotational structure of the fluorescence excitation spectrum of the $B\ (\nu' = 10) \leftarrow X\ (\nu'' = 0)$ transition of the van der Waals molecule HeI_2 has been measured and analyzed. The analysis indicates that the molecule has a nonlinear equilibrium structure with $R' = 4.79 \pm 0.22$ Å and $R'' = 4.47 \pm 0.13$ Å where R is the perpendicular distance from the helium atom to a line drawn through the iodine atoms.

(11) Van der Waals complexes between s-tetrazine and a number of light gases have been observed and characterized by laser spectroscopic studies of a free supersonic expansion of s-tetrazine in a helium carrier gas. The observed complexes are of the form X-s-tetrazine and X_2-s-tetrazine where X = He, H_2, and Ar. The spectra are consistent with the X species in both types of complexes being bound on or near the out-of-plane C_{2v} axis on the top and/or bottom of the s-tetrazine ring. For the He and H_2 complexes analysis of the rotational structure indicates that the van der Waals bond length is ~3.3 Å. The observed red shift of the 0-0 band of the $^1B_{3u} \leftarrow {}^1A_{1g}$ transition of all complexes relative to that of s-tetrazine indicates that a slightly stronger van der Waals bond exists in the excited state. Observed vibrational progressions for these complexes indicates the stretching frequency of the van der Waals bond in the excited state is 38.0, 95, and 110 cm^{-1} for the X = He, H_2, and Ar complexes, respectively. The 0-0 band origins of the $^{12}C_2{}^{14}N_4HD$, $^{12}C_2{}^{14}N_4D_2$, $^{12}C^{13}C^{14}N_2H_2$, and $^{12}C_2{}^{14}N_3{}^{15}NH_2$ isotopic species relative to that of $^{12}C_2{}^{14}N_2H_2$ are also reported.

(12) The van der Waals molecule ArI_2 has been produced in a supersonic expansion of I_2 in mixed argon-helium carrier gas, and its fluorescence excitation spectrum has been observed. Spectra of the complex are only observed when the iodine stretching vibration is excited to $v' \geq 12$ in the excited $\tilde{B}$ electronic state. Above this value the intensity of the van der Waals spectrum is observed to be an oscillatory function of the iodine vibrational quantum number. This behavior is attributed to competition between two decay channels in the excited state: vibrational predissociation with a cross section that increases monotonically with v', and electronic predissociation with a cross section that oscillates with v'. The spectral linewidth provides a lower limit of 3×10^{-11} sec for the lifetime of the excited state involved in the 0-15 transition.

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

18 19 REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. ~~REPORT NUMBER~~ AFOSR-TR-78-0677	2. GOVT ACCESSION NO.
3. ~~RECIPIENT'S CATALOG NUMBER~~ 9 1	
4. TITLE (and Subtitle) 6 Laser Spectroscopic Technique	5. ~~TYPE OF REPORT & PERIOD COVERED~~ Final Report. Jun[redacted] 1975 — 30 Nov[redacted] 1977
	6. ~~PERFORMING ORG. REPORT NUMBER~~
7. AUTHOR(s) 10 Lennard Wharton	8. CONTRACT OR GRANT NUMBER(s) 15 AFOSR-75-2853
9. PERFORMING ORGANIZATION NAME AND ADDRESS University of Chicago 5801 Ellis Ave. Chicago, Il 60637	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 61102F 16 2303/B1 17 B1
11. CONTROLLING OFFICE NAME AND ADDRESS Air Force Office of Scientific Research/NC Bolling AFB DC 20332	12. REPORT DATE 11 Mar[redacted] 1978
	13. ~~NUMBER OF PAGES~~ 5
14. MONITORING AGENCY ~~NAME &~~ ADDRESS(if different from Controlling Office) 12 6p.	15. SECURITY CLASS. (of this report) Unclassified
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release: distribution unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Laser spectroscopy
Supersonic Jet
van der Waals Molecules
NO_2, I_2He, NO_2He, NaAr, Tetrazine, ArI_2
Energy Distribution in Photoproducts
Vibrational Relaxation

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The design, development and exploitation of first and second generation apparatus for studying the spectroscopy of ultra cold molecules by laser induced fluorescence. This technique was the first joining of supersonic jets and laser optical spectroscopy for the simplification of complex optical spectra, for the observation of new van der Waals molecules, and for the observation of photo chemical processes.

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